January 2009

Guessing Harmonic Oscillator Wavefunctions Using Maple

Carl W. David
University of Connecticut, Carl.David@uconn.edu

Guessing Harmonic Oscillator Wavefunctions using Maple

C. W. David
Department of Chemistry
University of Connecticut
Storrs, Connecticut 06269-3060

(Dated: November 19, 2008)

I. SYNOPSIS

The guessing of eigenfunctions is not trivial at higher quantum numbers, no matter what the system being considered. Instead of guessing, one can employ a symbolic calculus progam (Maple in this case) to aid in the reasoning process.

II.

We assume a harmonic oscillator whose Hamiltonian is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{k}{2}x^2$$

or, in atomic units

$$-\frac{1}{2}\frac{\partial^2}{\partial x^2}+\frac{1}{2}x^2$$

and an trial function

$$\psi_{trial}=\left(x^4+\beta x^2+\gamma\right)e^{-\alpha x^2}$$

where β and γ [1] are to be determined when making this an eigenfunction of the Hamiltonian.

```
>  #temp ho n = 4 eigenfunctionality
>  restart;
>  psi := (x^4+beta*x^2+gamma_var)*exp(-alpha*x^2);
>  H_psi_minus_E := expand(-(hbar^2/(2*m))*diff(psi,x$2)
+ (k/2)*x^2*psi - E*psi);
>  term := collect(expand(exp(alpha*x^2)*H_psi_minus_E),x);
>  t6 := coeff(term,x,6);
>  result_alpha := solve(t6=0,alpha);#
>  term := subs(alpha=result_alpha[1],term);
>  H_psi_minus_E := subs(alpha=result_alpha[1],H_psi_minus_E);
>  print(‘attempting the next term ‘);
>  term := collect(expand(exp(result_alpha[1]*x^2)*H_psi_minus_E),x);
>  t4 := coeff(term,x,4);
>  result_E := solve(t4=0,E);#
>  term := subs(E=result_E,term);
>  H_psi_minus_E := subs(E=result_E,H_psi_minus_E);
>  print(‘attempting the next term ‘);
>  term := collect(expand(exp(result_alpha[1]*x^2)*H_psi_minus_E),x);
>  t2 := coeff(term,x,2);
>  result_beta := solve(t2=0,beta);#
>  term := subs(beta=result_beta,term);
>  print(‘final, gamma_var, term ‘);
>  result_gamma_var :=
solve(term=0,gamma_var);
```

$$\psi := (x^4+\beta\,x^2+gamma\_var)\,e^{(-\alpha\tilde{}\,x^2)}$$

This is a restatement of the wave function in more human readable form. Notice γ had to be re-written as gamma_var, since γ is an internal Maple defined quantity.

Next we apply the Hamiltonian, and in anticipation of the Schrödinger equation, we subtract $E\psi$, all in one fell swoop. In symbolic terms, we form:

$$(H_{op}-E)\,\psi=0$$

Typeset by REVTEX

$$H\_psi\_minus\_E := -\frac{6\,hbar^2\,x^2}{m\,e^{(\alpha\tilde{}\,x^2)}} - \frac{hbar^2\,\beta}{m\,e^{(\alpha\tilde{}\,x^2)}} + \frac{9\,hbar^2\,\alpha\tilde{}\,x^4}{m\,e^{(\alpha\tilde{}\,x^2)}} + \frac{5\,hbar^2\,\alpha\tilde{}\,x^2\,\beta}{m\,e^{(\alpha\tilde{}\,x^2)}} + \frac{hbar^2\,\alpha\tilde{}\,gamma\_var}{m\,e^{(\alpha\tilde{}\,x^2)}} - \frac{2\,hbar^2\,\alpha\tilde{}^2\,x^6}{m\,e^{(\alpha\tilde{}\,x^2)}} - \frac{2\,hbar^2\,\alpha\tilde{}^2\,x^4\,\beta}{m\,e^{(\alpha\tilde{}\,x^2)}} - \frac{2\,hbar^2\,\alpha\tilde{}^2\,x^2\,gamma\_var}{m\,e^{(\alpha\tilde{}\,x^2)}} + \frac{1}{2}\,\frac{k\,x^6}{e^{(\alpha\tilde{}\,x^2)}} + \frac{1}{2}\,\frac{k\,x^4\,\beta}{e^{(\alpha\tilde{}\,x^2)}} + \frac{1}{2}\,\frac{k\,x^2\,gamma\_var}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,x^4}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,\beta\,x^2}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,gamma\_var}{e^{(\alpha\tilde{}\,x^2)}}$$

Nest, we remove the common exponential term.

We wish then to demonstrate that our result is a polynomial in x. To do this, we collect terms in descending powers of x, purely for illustrative purposes. Since the l.h.s of this expression equals zero (making it a Schrödinger equation) we have:

$$term := (\frac{k}{2} - \frac{2\,hbar^2\,\alpha\tilde{}^2}{m})\,x^6 + (\frac{9\,hbar^2\,\alpha\tilde{}}{m} + \frac{k\,\beta}{2} - \frac{2\,hbar^2\,\alpha\tilde{}^2\,\beta}{m} - E)\,x^4 + (\frac{k\,gamma\_var}{2} + \frac{5\,hbar^2\,\alpha\tilde{}\,\beta}{m} - \frac{6\,hbar^2}{m} - \frac{2\,hbar^2\,\alpha\tilde{}^2\,gamma\_var}{m} - E\,\beta)\,x^2 - E\,gamma\_var - \frac{hbar^2\,\beta}{m} + \frac{hbar^2\,\alpha\tilde{}\,gamma\_var}{m}$$

We isolate the x^6 term's coëfficient next, preparing to declare that this coëfficient must be zero (as must the coëfficients of x^4, x^2 and x^0):

$$t6 := \frac{k}{2} - \frac{2\,hbar^2\,\alpha\tilde{}^2}{m}$$

Setting the coëfficient of x^6 equal to zero and solving, we get two solutions. The first of these is positive definite, and is the one corresponding to the eigenfunction assumptions made at the outset.

$$result\_alpha := \frac{\sqrt{k\,m}}{2\,hbar},\ -\frac{\sqrt{k\,m}}{2\,hbar}$$

$$term := (\frac{9\,hbar\,\sqrt{k\,m}}{2\,m} - E)\,x^4 + (\frac{5\,hbar\,\sqrt{k\,m}\,\beta}{2\,m} - \frac{6\,hbar^2}{m} - E\,\beta)\,x^2 - E\,gamma\_var - \frac{hbar^2\,\beta}{m} + \frac{hbar\,\sqrt{k\,m}\,gamma\_var}{2\,m}$$

There are two roots here, we choose the positive definite one.

$$H\_psi\_minus\_E := -\frac{6\,hbar^2\,x^2}{m\,e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} - \frac{hbar^2\,\beta}{m\,e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} + \frac{9}{2}\,\frac{hbar\,\sqrt{k\,m}\,x^4}{m\,e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} + \frac{5}{2}\,\frac{hbar\,\sqrt{k\,m}\,x^2\,\beta}{m\,e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} + \frac{1}{2}\,\frac{hbar\,\sqrt{k\,m}\,gamma\_var}{m\,e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} - \frac{E\,x^4}{e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} - \frac{E\,\beta\,x^2}{e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}} - \frac{E\,gamma\_var}{e^{(\frac{\sqrt{k\,m}\,x^2}{2\,hbar})}}$$

attempting the next term

$$term := \left(\frac{9\, hbar\, \sqrt{k\, m}}{2\, m} - E\right) x^4 + \left(\frac{5\, hbar\, \sqrt{k\, m}\, \beta}{2\, m} - \frac{6\, hbar^2}{m} - E\, \beta\right) x^2 - E\, gamma\_var - \frac{hbar^2\, \beta}{m} + \frac{hbar\, \sqrt{k\, m}\, gamma\_var}{2\, m}$$

Again, we remove the exponential. Then, we set the x^4 term's coëfficient equal to zero, to obtain, as it turns out in this particular method, the eignenergy:

$$t4 := \frac{9\, hbar\, \sqrt{k\, m}}{2\, m} - E$$

$$result\_E := \frac{9\, hbar\, \sqrt{k\, m}}{2\, m}$$

$$E_n = \frac{9}{2}\hbar\sqrt{\frac{k}{m}}$$

as expected, i.e.,$9 = 4 + \frac{1}{2}$!

$$term := \left(-\frac{2\, hbar\, \sqrt{k\, m}\, \beta}{m} - \frac{6\, hbar^2}{m}\right) x^2 - \frac{4\, hbar\, \sqrt{k\, m}\, gamma\_var}{m} - \frac{hbar^2\, \beta}{m}$$

$$H\_psi\_minus\_E := -\frac{6\, hbar^2\, x^2}{m\, e^{\left(\frac{\sqrt{k\, m}\, x^2}{2\, hbar}\right)}} - \frac{hbar^2\, \beta}{m\, e^{\left(\frac{\sqrt{k\, m}\, x^2}{2\, hbar}\right)}} - \frac{2\, hbar\, \sqrt{k\, m}\, x^2\, \beta}{m\, e^{\left(\frac{\sqrt{k\, m}\, x^2}{2\, hbar}\right)}} - \frac{4\, hbar\, \sqrt{k\, m}\, gamma\_var}{m\, e^{\left(\frac{\sqrt{k\, m}\, x^2}{2\, hbar}\right)}}$$

$$attempting\ the\ next\ term$$

$$term := \left(-\frac{2\, hbar\, \sqrt{k\, m}\, \beta}{m} - \frac{6\, hbar^2}{m}\right) x^2 - \frac{4\, hbar\, \sqrt{k\, m}\, gamma\_var}{m} - \frac{hbar^2\, \beta}{m}$$

$$t2 := -\frac{2\, hbar\, \sqrt{k\, m}\, \beta}{m} - \frac{6\, hbar^2}{m}$$

$$result\_beta := -\frac{3\, hbar}{\sqrt{k\, m}}$$

$$term := -\frac{4\, hbar\, \sqrt{k\, m}\, gamma\_var}{m} + \frac{3\, hbar^3}{m\, \sqrt{k\, m}}$$

$$final,\ gamma\_var,\ term$$

$$result\_gamma\_var := \frac{3\, hbar^2}{4\, k\, m}$$

We now redo the computation in "atomic units" which allows us to see more clearly (for most of us) what's going on. Thus, we set $\hbar \to 1$, $m = 1$, and $k = 1$.

```
>  psi := (x^4+beta*x^2+gamma_var)*exp(-alpha*x^2);
>  H_psi_minus_E := expand(-(1/2)*diff(psi,x$2)
+ (1/2)*x^2*psi - E*psi);
>  term := collect(expand(exp(alpha*x^2)*H_psi_minus_E),x);
>  t6 := coeff(term,x,6);
>  result_alpha := solve(t6=0,alpha);#
>  term := subs(alpha=result_alpha[2],term);
>  H_psi_minus_E := subs(alpha=result_alpha[2],H_psi_minus_E);
>  print(`attempting the next term `);
>  term := collect(expand(exp(result_alpha[2]*x^2)*H_psi_minus_E),x);
>  t4 := coeff(term,x,4);
>  result_E := solve(t4=0,E);#
>  term := subs(E=result_E,term);
>  H_psi_minus_E := subs(E=result_E,H_psi_minus_E);
>  print(`attempting the next term `);
>  term := collect(expand(exp(result_alpha[2]*x^2)*H_psi_minus_E),x);
>  t2 := coeff(term,x,2);
>  result_beta := solve(t2=0,beta);#
>  term := subs(beta=result_beta,term);
>  print(`final, gamma_var, term `);
>  result_gamma_var :=
solve(term=0,gamma_var);
>  psi := subs(alpha=result_alpha[2],E=result_E,beta
=
>  result_beta,gamma_var=
result_gamma_var,psi);
```

$$\psi := (x^4 + \beta\, x^2 + \mathit{gamma\_var})\, e^{(-\alpha\tilde{}\, x^2)}$$

$$\begin{aligned}\mathit{H\_psi\_minus\_E} := & -\frac{6\,x^2}{e^{(\alpha\tilde{}\,x^2)}} - \frac{\beta}{e^{(\alpha\tilde{}\,x^2)}} + \frac{9\,\alpha\tilde{}\,x^4}{e^{(\alpha\tilde{}\,x^2)}} + \frac{5\,\alpha\tilde{}\,x^2\,\beta}{e^{(\alpha\tilde{}\,x^2)}} + \frac{\alpha\tilde{}\,\mathit{gamma\_var}}{e^{(\alpha\tilde{}\,x^2)}} \\ & - \frac{2\,\alpha\tilde{}^2\,x^6}{e^{(\alpha\tilde{}\,x^2)}} - \frac{2\,\alpha\tilde{}^2\,x^4\,\beta}{e^{(\alpha\tilde{}\,x^2)}} - \frac{2\,\alpha\tilde{}^2\,x^2\,\mathit{gamma\_var}}{e^{(\alpha\tilde{}\,x^2)}} + \frac{1}{2}\,\frac{x^6}{e^{(\alpha\tilde{}\,x^2)}} + \frac{1}{2}\,\frac{x^4\,\beta}{e^{(\alpha\tilde{}\,x^2)}} \\ & + \frac{1}{2}\,\frac{x^2\,\mathit{gamma\_var}}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,x^4}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,\beta\,x^2}{e^{(\alpha\tilde{}\,x^2)}} - \frac{E\,\mathit{gamma\_var}}{e^{(\alpha\tilde{}\,x^2)}}\end{aligned}$$

$$\begin{aligned}\mathit{term} := & (\frac{1}{2} - 2\,\alpha\tilde{}^2)\,x^6 + (9\,\alpha\tilde{} + \frac{1}{2}\,\beta - 2\,\alpha\tilde{}^2\,\beta - E)\,x^4 \\ & + (\frac{\mathit{gamma\_var}}{2} + 5\,\alpha\tilde{}\,\beta - 6 - 2\,\alpha\tilde{}^2\,\mathit{gamma\_var} - E\,\beta)\,x^2 - E\,\mathit{gamma\_var} - \beta \\ & + \alpha\tilde{}\,\mathit{gamma\_var}\end{aligned}$$

$$\mathit{t6} := \frac{1}{2} - 2\,\alpha\tilde{}^2$$

$$\mathit{result\_alpha} := \frac{-1}{2},\, \frac{1}{2}$$

$$\mathit{term} := (\frac{9}{2} - E)\,x^4 + (\frac{5}{2}\,\beta - 6 - E\,\beta)\,x^2 - E\,\mathit{gamma\_var} - \beta + \frac{\mathit{gamma\_var}}{2}$$

$$\begin{aligned}\mathit{H\_psi\_minus\_E} := & -\frac{6\,x^2}{e^{(\frac{x^2}{2})}} - \frac{\beta}{e^{(\frac{x^2}{2})}} + \frac{9}{2}\,\frac{x^4}{e^{(\frac{x^2}{2})}} + \frac{5}{2}\,\frac{x^2\,\beta}{e^{(\frac{x^2}{2})}} + \frac{1}{2}\,\frac{\mathit{gamma\_var}}{e^{(\frac{x^2}{2})}} - \frac{E\,x^4}{e^{(\frac{x^2}{2})}} - \frac{E\,\beta\,x^2}{e^{(\frac{x^2}{2})}} \\ & - \frac{E\,\mathit{gamma\_var}}{e^{(\frac{x^2}{2})}}\end{aligned}$$

attempting the next term

$$\mathit{term} := (\frac{9}{2} - E)\,x^4 + (\frac{5}{2}\,\beta - 6 - E\,\beta)\,x^2 - E\,\mathit{gamma\_var} - \beta + \frac{\mathit{gamma\_var}}{2}$$

$$\mathit{t4} := \frac{9}{2} - E$$

$$\mathit{result\_E} := \frac{9}{2}$$

$$\mathit{term} := (-2\,\beta - 6)\,x^2 - 4\,\mathit{gamma\_var} - \beta$$

$$\mathit{H\_psi\_minus\_E} := -\frac{6\,x^2}{e^{(\frac{x^2}{2})}} - \frac{\beta}{e^{(\frac{x^2}{2})}} - \frac{2\,x^2\,\beta}{e^{(\frac{x^2}{2})}} - \frac{4\,\mathit{gamma\_var}}{e^{(\frac{x^2}{2})}}$$

attempting the next term

Notice that we were forced to choose the second root here, rather than our previous first root choice. Symbollic calculations sometimes have a mind of their own.

$$term := (-2\,\beta - 6)\,x^2 - 4\,gamma\_var - \beta$$
$$t2 := -2\,\beta - 6$$
$$result\_beta := -3$$
$$term := 3 - 4\,gamma\_var$$
$$final,\ gamma\_var,\ term$$
$$result\_gamma\_var := \frac{3}{4}$$
$$\psi := (x^4 - 3\,x^2 + \frac{3}{4})\,e^{(-\frac{x^2}{2})}$$

This last result, the interpreted wave function with constants shown, is a variant on the textbook form, and shows that indeed the Hermite polynomial multipled by an appropriate exponential, is the desired eigenfunction.

All's well in the world.

---

[1] Sad to say, γ is a variable internal to Maple, so we need to define something which won't be handled improperly by Maple.